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"The Inorganic Ozonides"

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The Inorganic Ozonides

The recent search for compounds which can act as solid state storage media for oxygen has engendered considerable interest in compounds containing oxygen in unfamiliar oxidation states, such as the superoxides and ozonides. In this paper it is intended to present a review of the chemistry of the inorganic ozonides and point out those areas where additional research is necessary in order to make our knowledge of these important compounds more nearly definitive.

The Discovery of Ozonides

Reactions between ozone and alkali metal hydroxides have been of interest to investigators for over one hundred and fifty years. Mellor (1) reports that as early as 1844, C. F. Schonbein (2) found that when ozone is passed through 40% aqueous potassium hydroxide solution "something forms" which gives a blue color to potassium iodide-starch mixtures. Würtz (3) in 1868, described the preparation of a stable orange solid when ozone is passed over powdered sodium or potassium hydroxide. In 1902, von Baeyer and Villiger (4) showed that ozone passed through a "strongly cooled solution of potash lye" forms an orange-brown solution, the color disappearing as the solution is allowed to warm to room temperature. Similar observations were made with solid potassium hydroxide. The work cited above is among the earliest recorded evidence for what we now recognize to be metal ozonides, $M^+O_3^-$, colored, paramagnetic, ionic solids.

Further work in the early history of inorganic ozonide chemistry was carried out by Traube (5). He reported that when 5 to 7% ozone in oxygen is passed over powdered potassium hydroxide, a mixture is formed containing small amounts of KOH, " K_2O_4 ," and "another bright yellow-red compound." This "other compound" was the chief product and slowly decomposed near room temperature to " K_2O_4 " which subsequently gave an equal number of moles of oxygen and hydrogen peroxide. These results indicate the preparation of potassium ozonide and potassium superoxide. Later, in 1916, Traube (6) also prepared deeply colored rubidium and cesium "ozonates" by passing ozone over the hydroxides. Analogously to the potassium compounds, the rubidium and cesium "ozonates" liberated oxygen but no hydrogen peroxide on contact with water soon after preparation. However, on standing, the "ozonates" decolorized and yielded oxygen and hydrogen peroxide in equivalent amounts. The decomposition was retarded by refrigeration of the sample. Although the true nature and structure of the major product of Traube's reactions was unknown to him, his careful work was the first indication that

the "ozonates," as he called them, decomposed at room temperature and above to the corresponding tetroxide, M_2O_4 , which we now recognize to be the superoxide, MO_2 .

Between 1907 and 1913 Manchot and Kampschulte (7) and Manchot (8) carried out work of significance, preparing yellow colored compounds of sodium, rubidium, cesium, barium, and calcium by a reaction between ozone and the respective hydroxides. However, in contrast to Traube's observations, they reported that the alkali metal products were apparently quite thermally stable, their yellow color disappearing only upon heating to approximately 100°C in the presence of 8-9% ozone. The stability increased with increasing atomic weight of the alkali metal. Due to the differences in experimental conditions under which the observations of stability were made by Manchot and Traube it is difficult to attach significance to the variance of their results. However, it is significant, as will be pointed out below, that modern workers are also at variance concerning the stabilities of the ozonides.

Manchot and Kampschulte (7) placed strong emphasis on the role of water in the ozone-hydroxide reactions. They stated that the presence of water hinders or prevents the formation of colored products. This claim is in conflict with the more recent studies of Whaley and Kleinberg (9) who reported that water is necessary in order to catalyze the reaction of ozone with metal hydroxides. Strecker and Thienemann (10), moreover, found that the reaction of ozone with alkali metals dissolved in liquid ammonia was accelerated by the presence of small amounts of moisture. They, also in agreement with Manchot, made note of the fact that the ease of formation and stability of the colored solids increase in the order: sodium, potassium, rubidium, and cesium. This order of stability is the same as found with the alkali metal superoxides, $M^+O_2^-$, and is to be expected on the basis that as the ionic radii of the metal ions become larger a more stable crystal lattice results. The order of ozonide stability has also been confirmed by later workers (28). It is of interest to point out that precipitates of "barium and calcium ozonides" were apparently obtained in liquid ammonia, but that these compounds completely decomposed as soon as the ammonia was evaporated.

It is obvious that the true nature of the colored compounds formed was not well understood by the early workers. Traube first suggested the formula K_2O_7 (5) and later $(KOH)_2 \cdot O_2$ (6) for what recent evidence (21) supports to be KO_3 , potassium ozonide. Bach (11), in 1902, discussed the possibility that the potassium ozonide of von Baeyer and Villiger (4) was an addition product of ozone and potassium with the formula KO_3H .

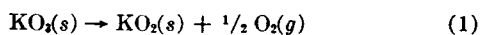
Potassium tetroxide and K_2O_4 were in common use prior to 1931 as the name and formula for potassium superoxide, KO_2 12-14. In 1935 Weiss (15) postulated that the yellow color appearing in 40% KOH at -40°C in contact with ozonized oxygen is due to superoxide. However, under the same conditions McLachlan, Symons, and Townsend (16) detected ozonide formation but no superoxide.

Fichter and Bladergroen, in 1927, published the results of interesting investigations in which "potassium ozonate" was obtained by passing fluorine through concentrated potassium hydroxide solution at -20°C (17). The "ozonate" was reported to be a yellow to brown solid which abruptly exploded. Fichter and Bladergroen identified their product with that of von Baeyer and Villiger (4), and accounted for its formation by postulating a reaction between potassium hydroxide and fluorine to form ozone. This reaction is analogous to the ozone-forming reaction between water and fluorine, which was discussed in the same paper. These authors also reported that the "ozonate" is formed when fluorine is passed over solid potassium hydroxide.

Potassium ozonide was also apparently obtained by Riesenfeld and Reinhold (18) by the electrolysis of potassium hydroxide solution at -40° , by LeBlanc and Zellmann (19) at -25° , and by Rius y Miro (20) at 2° to 4° .

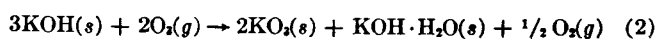
Recent Developments—the Russian Work

The impetus to the modern interest in inorganic ozonide chemistry was supplied by the work of the Russian investigators Kazarnovskii, Nikol'skii, and Abletsova (21). In 1949 they reported the preparation of 93% pure KO_3 by exposing dry powdered KOH to oxygen containing 6-8% ozone at -10 to -15°C . The product was extracted with liquid ammonia to yield red-brown needles of KO_3 . They found that KO_3 decomposes completely in 11 days in the following manner:



At higher temperatures, i.e. $50-60^\circ$, the decomposition is complete in about 30 minutes. Kazarnovskii, *et al.* also determined the magnetic susceptibility of KO_3 and found it to have a magnetic moment of 1.67 Bohr magnetons. This value is in good agreement with the theoretical value of 1.73, corresponding to one unpaired electron, and tends to confirm the formula for potassium ozonide as KO_3 , as the O_3^- ion does have one unpaired electron and probably involves a resonating structure containing a three electron bond.

For the over-all formation reaction, these investigators offered the following:

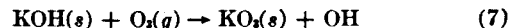


and they assumed it to proceed according to the following steps:

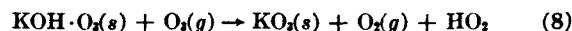


This mechanism remains to be verified. Nikol'skii,

Kazarnovskaya, Bagdasar'yan, and Kazarnovskii continued the study of potassium ozonide, and in a 1950 paper (22) reported the heat of formation of KO_3 to be 62.1 ± 0.9 kcal/mole and calculated the thermodynamic properties ΔH° , ΔS° , and ΔF° for the reaction



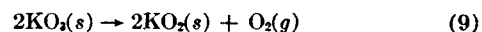
to be 15.4 kcal/mole, -3.2 e.u., and 16.35 kcal/mole, respectively. On the basis of these values they concluded that reaction (7) is thermodynamically excluded as a step in the formation process, and suggested the following mechanism as a possibility:



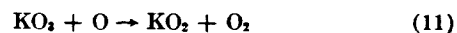
Nikol'skii, *et al.*, using the X-ray crystallographic data of Zhdanov and Zvonkova (23), calculated the lattice energy of KO_3 to be 149 kcal/mole. Using this value along with their value for the heat of formation of KO_3 , they were able to calculate a value of 66.5 kcal/mole for the electron affinity of the ozone molecule. Pritchard (24) points out that although 66.5 kcal/mole appears to be a surprisingly high value for the electron affinity of ozone, approximately three times larger than the electron affinity of oxygen, it is not an unreasonable value. To support this view he points out the similarity of ozone to sulfur dioxide and selenium dioxide whose electron affinities are 64.5 and 53 kcal/mole, respectively. It is also of interest to point out the case of the electron affinity of the azide radical versus the nitrogen molecule. The electron affinity of N_3 as determined by Franklin, *et al.* (25) is 71.9 kcal/mole, whereas the nitrogen molecule appears to have essentially no affinity for electrons.

The Question of Ozonide Stability

Nikol'skii, *et al.* (22) studied the decomposition reaction

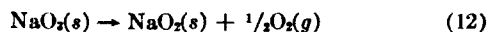


and found ΔH° , ΔS° , and ΔF° to be -11.6 kcal/mole, 33 e.u., and -21.63 kcal/mole, respectively. Later magnetic and kinetic studies on this decomposition by Kazarnovskii, Raikhshtein, and Bykova (26,27) established that the reaction involves atomic oxygen as an intermediate and proceeds according to



It would be of considerable interest to carry out a complete thermal decomposition study of KO_3 in order to establish whether or not solid solutions or other oxide phases form in the composition range between KO_3 and KO_2 . The evidence at hand would indicate that the decomposition reaction represents a two component, single phase system.

In 1951, Nikol'skii, Bagdasar'yan, and Kazarnovskii (28) reported the preparation of the ozonides of sodium (colored red), rubidium (orange), and cesium (brown). Sodium ozonide was prepared at -55° using anhydrous NaOH and 8-9% ozone in oxygen. The material was extracted at -50° with liquid ammonia, and upon evaporation of the ammonia a dark red powder was obtained which was found to be 90% NaO_3 . At room temperature the following reaction was complete in approximately 53 hours:



During the course of the reaction, the solid changed color from dark red to yellow, which is the color usually associated with NaO_2 . Thus, according to the Russian investigators, the stability of NaO_3 (completely decomposed in 53 hours) is much less than that of KO_3 (completely decomposed in 11 days).

In 1951, Whaley and Kleinberg (9) also prepared NaO_3 , KO_3 , and CsO_3 . Their results are in essential agreement with the Russian results but there are significant differences, especially as pertaining to the results on NaO_3 . Whaley and Kleinberg report that no decomposition of NaO_3 to NaO_2 was obtained. This is in direct contradiction to the Russian findings. In addition, Whaley and Kleinberg report that NaO_3 is apparently stable at room temperature, no decomposition being noted in samples which had stood for 18 months. This is to be compared with the Russian result which claims complete decomposition of NaO_3 in 53 hours. The NaO_3 product on which Whaley and Kleinberg made their studies was prepared at room temperature. They found that in contrast to the Russian result on NaO_3 (prepared at -50 to -60°C), their product was insoluble in liquid ammonia. This observation of Whaley and Kleinberg was confirmed by McLachlan, Symons, and Townsend (16).

Solomon and Kacmarek (29) investigated the apparent discrepancy concerning the solubility of sodium ozonide. They concluded that one possibility for the varying solubility and stability characteristics of sodium ozonide is that it exists in two crystalline forms, one being soluble in liquid ammonia and unstable at room temperature, and the other being insoluble and stable. Analogously, potassium ozonide has been reported to exist in two forms, the tetragonal potassium bifluoride lattice of potassium azide observed by Zhdanov and Zvonkova (23) and the monoclinic potassium nitrite structure, observed by Solomon and Kacmarek (29). Smith (30) considering the X-ray crystallographic data on KO_3 of Zhdanov and Zvonkova, predicted the existence of KO_3 in two crystalline forms. The above studies shed some light on the reason for the conflicting results of the Russian investigators and Whaley and Kleinberg.

Although sodium, potassium, rubidium, and cesium ozonides were synthesized, the Russian investigators were unsuccessful in their attempts to produce lithium ozonide. They offer a thermodynamic argument to explain the lack of success. By assuming the rate determining step for the formation reaction to be



Nikol'skii, Bagdasar'yan, and Kazarnovskii (28) calculated for M =potassium, $\Delta F^\circ_{298} = -28$ kcal/mole. On the basis of the studies by Zhdanov and Zvonkova the crystal structure of KO_3 was shown to bear great resemblance to that of KN_3 . Extending this analogy to the point of assuming the same degree of crystal structure correspondence between NaO_3 and NaN_3 , and RbO_3 and RbN_3 , Nikol'skii, *et al.*, were able to estimate lattice energies for the various alkali metal ozonides and thereby arrive at the thermodynamic values shown in the table for the rate determining step, equation (13).

Thus, on the basis of the Russian data and reasoning,

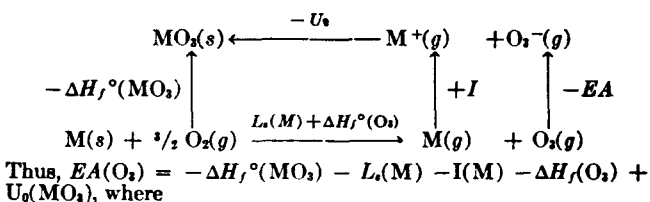
the formation of lithium ozonide is not thermodynamically favored. However, these data cannot as yet be considered definitive.

In a very fine paper, Smith (30) reexamined the X-ray data of Zhdanov and Zvonkova. Smith suggested that the O_3^- ion may not be linear as is the N_3^- ion, but may in fact be bent. McLachlan, Symons, and Townsend (16) came to the same conclusion on the basis of the absence of detectable asymmetry from the ESR spectrum of sodium ozonide. The validity of the thermodynamic values (see table) estimated by the Russians is thus open to question.

Thermodynamic Properties Calculated for Reaction (13),
 $\text{MOH} + 2\text{O}_2 \rightarrow \text{MO}_3 + \text{HO}_2 + \text{O}_2$ (28)

<i>M</i>	$-\Delta H^\circ$, kcal/mole	ΔF°_{298} , kcal/mole
Li	-12	11
Na	10	-11
K	27	-28
Rb	28	-29
Cs	31	-32

An interesting question emerging from Smith's paper is that of a possible discrepancy in the reported value for the electron affinity of ozone, 66.5 kcal/mole (22). Once the family of alkali metal ozonides is successfully prepared in essentially pure form, and the heats of formation and lattice energies determined, it should be possible to derive a good value for the electron affinity of the ozone molecule by the application of the Born-Haber cycle, i.e.,



$EA(\text{O}_3)$ = electron affinity of ozone

ΔH_f° = heats of formation

M = alkali metal

L_s = latent heat of sublimation of the alkali metal

I = ionization potential of the alkali metal

U_0 = lattice energy of the alkali metal ozonide

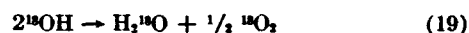
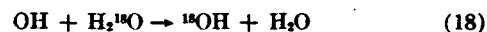
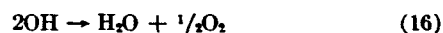
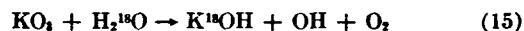
The Reaction of Ozonides with Water

All of the investigations carried out to date are in essential agreement that the ozonides react with water to form oxygen and hydroxide, i.e.,



The practicality of ozonides as solid state storage media for oxygen is readily evident.

In 1957, Kazarnovskii, Lipichin, and Tikhomirov (31) studied the isotopic exchange of oxygen between the free hydroxyl radical and water, and they offered the following steps in order to account for reaction (14).



They propose that not more than 15% of the OH forms H_2O_2 .

Tetramethylammonium Ozonide

It might be expected that very strong bases, in general, can form ozonides. In support of this is the recent preparation and characterization of tetramethylammonium ozonide, $(\text{CH}_3)_4\text{N}^+\text{O}_3^-$, by Solomon, *et al.* (32). This compound was first prepared in 1929 by Traube and Kuhbier (33) as a stable red solid by ozonating tetramethylammonium hydroxide. Using a similar method, Solomon, *et al.*, obtained a product that was unstable at room temperature. The visible spectra, solubility in liquid ammonia, and heat of formation of tetramethylammonium ozonide were established. The interesting observation was made that the stability of this particular ozonide decreased as the purity of the sample increased, pure tetramethylammonium ozonide decomposing completely in 48 hours to oxygen, trimethylamine, water, tetramethylammonium hydroxide, tetramethylammonium formate, and tetramethylammonium carbonate. It is of interest to speculate on the role this member of the ozonide family may be made to play as an intermediate in the synthesis of other ozonide compounds.

Ammonium Ozonide

The work of Manchot (7) and Manchot and Kampschulte (8) between 1907 and 1913 provided the first evidence that ammonium ozonide could exist. They found that when dilute ozone was passed into liquid ammonia a deep orange-red liquid was obtained, whose color persisted until the liquid was warmed. They found that the color was most intense at -70°C , and faded considerably at -60°C . Later, Strecker and Thieneman (10) also observed a transitory red color upon passing dilute gaseous ozone into liquid ammonia, although the product isolated was mostly ammonium nitrate.

Recently, Solomon, Hattori, Kacmarek, Platz, and Klein (34) have prepared low yields of ammonium ozonide $(\text{NH}_4^+\text{O}_3^-)$ by the reaction between liquid ammonia and dilute ozone at approximately -100°C . Ammonium ozonide was found to be thermally unstable above -126°C , decomposing to ammonium nitrate, oxygen, and water. The visible absorption spectrum of ammonium ozonide was shown to resemble those of sodium, potassium, rubidium, cesium, and tetramethylammonium ozonides in the region of 450 m μ .

Studies of the ozonides and the mechanisms of their chemical reactions will help to shed light on the role played by the conjugate acid of the O_3^- ion in a number of important inorganic free radical mechanisms. Essentially, the same can be said today as was said by Smith in 1956 (30), i.e., the role of the HO_3 radical has received little attention as an intermediate in chemical processes. Benson (35) has pointed out that on the basis of thermodynamic evidence HO_3 is unstable with respect to decomposition into HO and O_2 and is, therefore, not a utilizable intermediate. However, Symons has offered evidence for the formation of the O_3^- species based on electron spin resonance studies of the reactions between H_2O_2 and aqueous NaOH (16). Also, Forscheimer and Taube (36) have suggested a

role for the O_3^- species in the exchange reaction between water and molecular oxygen, and Wilmarth (37) has reported the formation of ozone from the thermal decomposition of persulfate ion ($\text{S}_2\text{O}_8^{2-}$) and has postulated that the ozone results from a free radical oxidation of O_3^- or HO_3 . It is obvious that a great deal of information is necessary in order to clarify the mechanisms of inorganic free radical reactions, and it is hoped that the availability of stable inorganic ozonides will be useful in this respect.

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